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Intensification of esterification reaction of lactic acid with iso-propanol using pervaporation reactor

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Abstract

Pervaporation in recent years has received strong attention from industry as a novel, energy-efficient and environmental-friendly separation technology.Pervaporation reactor is a new technology to enhance conversion in reversible esterification reactions. In present work, polyvinyl alcohol-polyether sulfone (PVA-PES) composite hydrophilic membrane was used for pervaporation-assisted esterification of lactic acid with iso-propanol. Experimental work of esterification of lactic acid with iso-propanol coupled with pervaporation was carried out. Effect of various parameters, such as, initial mole ratio of iso-propanol over lactic acid, the ratio of the effective membrane area over the volume of reacting mixture, process temperature and catalyst concentration on the performance of pervaporation reactor were discussed.The presented data can be extended for study and design of pervaporation reactor for similar kind of reactions.

Keywords: pervaporation reactor, esterification, lactic acid, iso-propanol, experimental

Nomenclature	
S	Surface area of membrane (m^2)
V	Volume of reacting mixture (m^3)
T	Temperature (^oC)
C_c	Catalyst concentartion ($kmol/m^3$)
R	Initial molar reactant ratio

1. Introduction

Esterification of carboxylic acids and alcohols is a typical example of an equilibrium limited reaction that produces water as by product. Due to thermodynamic equilibrium condition the conversion is generally low and increases cost by using a large excess reactant for shifting the position of equilibrium [1].Therefore to increase the conversion and shift the position of the equilibrium by removing the water pervaporation reactor is a very useful technology for this process. The reaction studied for the application of pervaporation reactor is an esterification of lactic acid with isopropanol to give isopropyl lactate and water.

$$C_3H_6O_3 + C_3H_8O \leftrightarrow C_6H_{12}O_3 + H_2O$$

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Pervaporation enhanced reactors are expected to provide a promising alternative due to rate controlled separation process, energy consumption is generally low as compared to distillation, and pervaporation can be operated at a temperature that matches the optimal temperature for reaction with an appropriate membrane. The last feature is particularly important for esterifications due to temperature constraints [2].

Pervaporation membrane reactors have been studied for esterification of acetic acid and iso-propanol [3], oleic acid and ethanol [4, 5], propionic acid and propanol [6, 7], tartaric acid and ethanol [8], oleic acid and butanol [9] and valeric acid and ethanol [10] with various acids or lipases as catalysts. In some cases the membrane itself can be catalytically active [11].A very few work has been available on pervaporation reactor for esterification reactions of lactic acid with iso-propanol [12-15].

In present paper experiments were conducted for esterification of lactic acid with iso-propanol coupled with pervaporation and without pervaporation. Also the effect of various process variables, such as process temperature, initial mole ratio of iso-propanol over lactic acid, and the ratio of the effective membrane area over the volume of reacting mixture, catalyst content on the performance of pervaporation reactor for esterification reaction were discussed.

2. Experimental

2.1. Membrane

Polyvinyl alcohol-polyether sulfone (PVA-PES) composite type membrane was used in membrane test cell of pervaporation reactor (supplied by Permionics Membranes Pvt. Ltd., India, size of test cell: 240 mm x 180 mm x 25 mm, and MOC of test cell SS-316) with active membrane area 0.0155 m^2.

2.2. Differential scanning calorimetry (DSC)

The melting point of polyvinyl alcohol-polyether sulfone (PVA-PES) composite type membrane was measured with SIICO AS-3 DSC-7020 differential scanning calorimetry. The samples for DSC analysis were 10-20 mg; the heating and cooling rate was 15 ºC min^{-1} over a temperature range of 50-350 ºC and the carrier gas was nitrogen. The samples were placed in an aluminium pan, and an empty aluminium pan was used as a reference. The melting point was measured from the highest position at the peak of the heating cycle. The melting point of PVA-PES composite membrane measured with DSC was 250^0C and the results are shown in Fig.1.

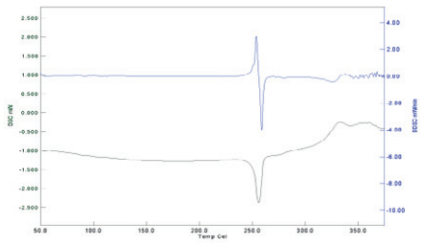

Fig. 1. Differential Scanning Calorimetric (DSC) analysis of membrane of PVA-PES

2.3. Apparatus

The reaction and separation were carried out in a laboratory-scale pervaporation reactor supplied by Permionics Membranes Pvt. Ltd., India (Fig. 2).

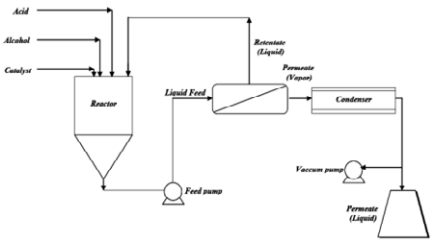

Fig. 2. Typical diagram of pervaporation reactor (PVR)

2.4. Esterification

Analytic grade reagents aqueous lactic acid (88-92%, Qualigens, India) and iso-propanol (99%, Qualigens, India) were used. Esterification experiments utilized the equivalent of mole lactic acid and mole of iso-propanol, giving a mole ratio of iso-propanol to lactic acid as 1:1. Experiments were carried out with and without catalyst. Sulphuric acid (99.9%, Aldrich, India) was used as a catalyst.

2.5. Analysis

The permeate composition and the amount of product in reaction mixtures were obtained by titration with 0.125 N NaOH. Few titrations were performed in triplicate and results were obtained in the range of ± 4%, which is acceptable.

3. Results and Discussion

An esterification with and without pervaporation were carried out in a laboratory-scale pervaporation reactor. Effect of various parameters, such as process temperature (50- 90^{o}C), initial mole ratio of iso-propanol over lactic acid (1-1.5), the ratio of the effective membrane area per unit volume of reacting mixture were carried out both with and without catalyst. Catalyst concentrations were varied from 0.105- 0.525 kmol/m^3 on the performance of pervaporation reactor were carried out. The results are discussed in further section.

From Fig**. 3** it was found that pervaporation enhanced the conversion than without pervaporation. In case of pervaporation considerable enhancement was observed and the conversion was increased from its equilibrium value of 51% to 86% using a PVA-PES membrane. This membrane was the most selective one for water transport of membranes used in this work [16]. If the removal of water is indeed the major mechanism for the enhancement of yield, same was observed in these experiments.

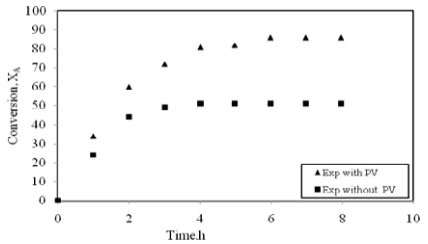

Fig. 3. Comparison of experimental results for lactic acid conversion (T= 90°C; C_C = 0.422 kmol/m^3; R =1.4; S/V = 15.19 m^2/m^3): with PV (▲), without PV (■).

The variation of water concentration in the reacting mixture as a function of time for the reaction without PV and the PV-aided reaction is displayed in Fig. 4. It reflected that the water content for the reaction without PV was higher than for the PV-aided reaction due to water removal by PV.

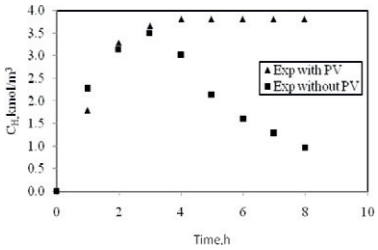

Fig. 4. Comparison of experimental results of water concentration for esterification with and without pervaporation (T= 90°C; C_C = 0.422 kmol/m^3; R = 1.4; S/V = 15.19 m^2/m^3): with PV (▲), without PV (■).

From Fig 5, it can be observed that increased in temperature increased the conversion. An increase in temperature induced not only an acceleration of esterification but also acceleration in pervaporation. Water production rate was higher at higher temperature than in a lower temperature (Fig. 5). Water concentration had a higher maximum value for a higher process temperature, so water content increased faster during the earlier reaction stage due to a slower backward reaction rate; while decreased faster later due to a higher backward reaction rate [17].

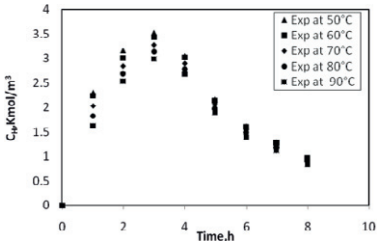

Fig. 5. Effect of change in temperature on water concentration (R = 1.4; C_C = 0.422 kmol/m^3; S/V = 15.19 m^2/m^3): T = 50°C (■), T = 60°C (●),T = 70°C (◆),T = 80°C (■),T = 90 °C (▲).

Catalyst concentration may be an alternative way to accelerate ester production. In view of this, the catalyst concentartion was varied from 0.105 kmol/m^3 to 0.525 kmol/m^3.The experimental results for conversion of lactic acid and water content during pervaporation process over various catalyst concentrations were presented in Fig. 6. It can be seen that as concentration of catalyst increased conversion increased. But a higher concentartion of catalyst then percentage enhancement in conversion is not much significant (< 4%).

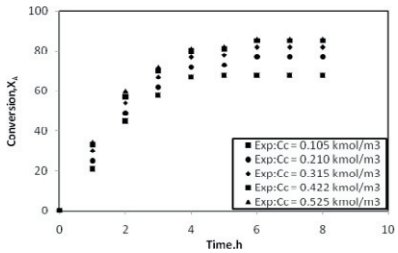

Fig. 6. Effect of change in catalyst concentration on conversion of lactic acid (T=90°C; R=1.4; S/V = 15.19 m^2/m^3): C_C = 0.105 kmol/m^3 (■), C_C = 0.210 kmol/m^3 (●), C_C = 0.315 kmol/m^3 (◆), C_C = 0.422 kmol/m^3 (■), C_C = 0.525 kmol/m^3 (▲).

Fig. 7.depicts the effect of initial molar reactant ratio on the lactic acid conversion. The reactant ratio was varied from 1 to 1.5 for fixed values of the other parameters. The higher conversion of lactic acid 86% was observed for higher ratios. It can be found that R played a part in reaction rate but exerted no effect on kinetics of PV. Here, water production rate is decreased with the increase of R and caused the maximum amplitude in water content lower at a higher R. The water contents in the reactor were lower for a higher R during the process, which was for the most part attributed to that R played no role in the kinetics of PV.

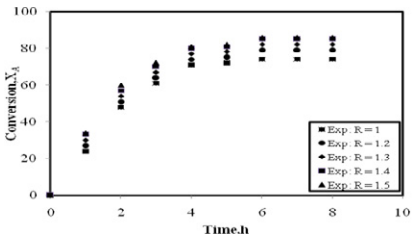

Fig. 7. Effect of change in ratio of initial reactants on conversion of lactic acid (T = 90°C; C_C = 0.422 kmol/m^3; S/V = 15.19 m^2/m^3): R = 1 (■), R = 1.2 (●), R =1.3 (◆), R = 1.4 (■), R = 1.5 (▲).

4. Conclusion

Experiments for esterification of lactic acid with iso-propanol coupled with and without pervaporation were carried out. The performance of pervaporation reactor was analyzed by studying effect of various parameters such as temperature, catalyst concentration, and reactant ratio. In this study pervaporation considerable enhancement was observed and the conversion of lactic acid was increased from its equilibrium value of 51% to 86% using a PVA-PES membrane as compared to conventional reactor. The presented data can be extended for study and design of pervaporation reactor for similar kind of reactions.

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